

Storage and cycling performance of Stoichiometric spinel at elevated temperatures

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Received 23 June 2000; received in revised form 2 January 2001; accepted 13 January 2001

Abstract

LiMn_2O_4 has been synthesized using LiOH and Mn_3O_4 for 20 h in air by the melt-impregnation method. It showed pure X-ray diffraction (XRD) patterns without any impurities at 750~900°C. This material exhibited a large 3.2 V plateau in its discharge curve when synthesized above 800°C. The 3.2 V plateau showed a strong relation with the oxygen deficiency in the spinel structure, which means a degree of oxygen deficiency of the LiMn_2O_4 spinel. We confirmed that the oxygen deficiency and Mn dissolution are very important factors for inducing a capacity loss in the stoichiometric spinel at elevated temperature. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: LiMn_2O_4 ; 3.2 V plateau; Oxygen deficiency; Capacity loss; Mn dissolution

1. Introduction

In the view of the economic and environmental advantages, there is no question that the LiMn_2O_4 spinel will be used as a cathode material for lithium-ion batteries instead of LiCoO_2 currently commercialized if the problem associated with the capacity fading upon cycling and storage at elevated temperature could be solved. However, LiMn_2O_4 still showed significant capacity fading at high temperature and poor cycleability when it was cycled over a wide voltage range for increasing the energy density.

Many research groups had reported some reasons which induced the capacity loss of the LiMn_2O_4 spinel in the 4 V region. [1,2] In our previous paper [3], we also reported that capacity loss during cycling of the LiMn_2O_4 at room temperature occurred only in the high voltage region and it was mainly caused by the unstable two-phase structure in the high voltage region for lithium ion insertion/extraction. Additionally, we have demonstrated that both the change in the crystal structure and the dissolution of Mn into the electrolyte are major factors responsible for the capacity loss at elevated temperature [4]. These two factors are critically dependent on the operating temperature.

In this paper, we synthesized a series of spinel compounds at different calcination temperatures and report the effect of

the oxygen deficiency in the stoichiometric LiMn_2O_4 spinel at different temperatures.

2. Experimental

The LiMn_2O_4 samples were synthesized using LiOH and Mn_3O_4 by the melt-impregnation method. The mixture of starting materials was precalcined at 470 and 530°C for 5 h in air, followed heating from 600 to 1000°C for 20 h.

The powder X-ray diffraction (XRD, Rint 1000, Rigaku) using $\text{Cu K}\alpha$ radiation was performed in order to identify the crystalline phase of the materials. The soaking test was conducted in a 1 M LiPF_6 -ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:2 by volume) solution for 1 or 2 weeks. A 3 g amount of the spinel powder was used along with 30 ml of electrolyte. They were placed in a Teflon bottle for a week at 50, 60 and 70°C. The amount of dissolved Mn ions in the electrolyte was analyzed by atomic adsorption spectroscopy. The electrochemical characterizations were performed using CR2032 coin-type cells. The cathode was 20 mg of accurately weighed active material and 13 mg of conductive binder. It was pressed on a 25 mm² stainless steel mesh used as the current collector at 300 kg/cm² and then dried at 200°C for 5 h in an oven. This cell consisted of a cathode and a lithium metal anode (Cyprus Foote Mineral Co.) separated by a porous polypropylene film as the separator (Celgard 3401). The electrolyte used

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was the same as that used in the soaking test. The charge and discharge current densities were 0.4 mA/cm² with a cut-off voltage of 3.5–4.3 V (versus Li/Li⁺).

3. Results and discussion

LiMn_2O_4 has been synthesized at 600–1000°C for 20 h in air. It showed a pure spinel phase without any impurities from 750 to 900°C except for Mn_2O_3 and Mn_3O_4 impurities that were detected in the low temperature region (600–700°C) and high temperature region (950–1000°C), respectively.

Fig. 1 shows the charge/discharge curves of the LiMn_2O_4 spinel which were synthesized at the different temperatures. The spinel powder obtained at 800°C showed the typical voltage profile of stoichiometric LiMn_2O_4 , such as the 4.0 V and 4.15 plateaus in the 4 V region, and exhibited a high discharge capacity above 130 mAh/g in the first cycle. This compound had the smallest 4.4 V plateau ($C_{4.4}\text{ v}$) and the smallest 3.2 V plateau ($C_{3.2}\text{ v}$) among the three samples. We also found that the $C_{4.4}\text{ v}$ and $C_{3.2}\text{ v}$ increased as the calcination temperature increased.

To investigate this phenomenon, the amount of Li and Mn in the four samples obtained at different temperatures (750–900°C) were analyzed using atomic adsorption spectroscopy. The oxygen content was determined by the infrared adsorption method using oxygen analyzer of LECO Co. (USA) model RO-416DR [5]. The LiMn_2O_4 obtained at 750°C showed an oxygen-rich spinel ($\text{Li}_{1.001}\text{Mn}_{1.999}\text{O}_{4.001}$) while the other three samples obtained at higher temperatures showed oxygen deficiency spinels as shown in Fig. 1. Therefore, there might be some relations between the two plateaus and the calcination temperatures.

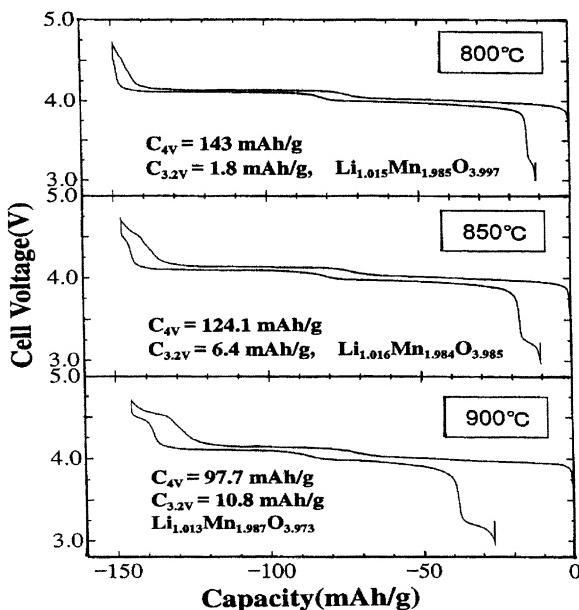


Fig. 1. The first charge/discharge curves of LiMn_2O_4 spinel obtained at different calcination temperatures.

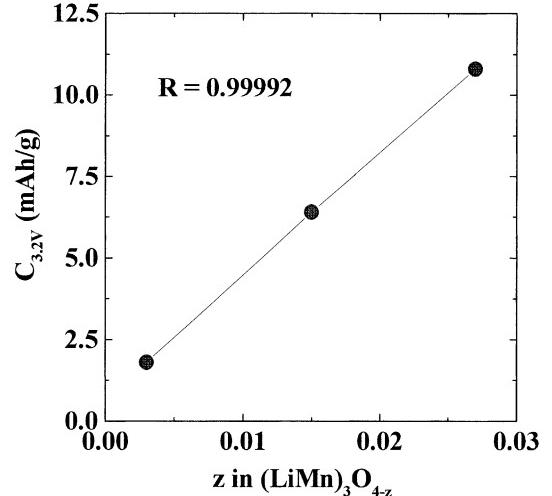


Fig. 2. Relation between $C_{3.2}\text{ v}$ and oxygen deficiency content (z).

Fig. 2 shows the relation between $C_{3.2}\text{ v}$ and the oxygen deficiency content (z). The value of $C_{3.2}\text{ v}$ increases with increasing oxygen deficiency. Furthermore, it shows a very clear relation between $C_{3.2}\text{ v}$ and the oxygen deficiency content. This means that the calcination of LiMn_2O_4 at high temperature induces an oxygen deficiency in the spinel structure and the amount of the 3.2 V plateau can represent the degree of oxygen deficiency in the spinel structure. Therefore, the $C_{3.2}\text{ v}$ value that results from the oxygen deficiency can be used as an indicator for the degree of oxygen deficiency in the LiMn_2O_4 spinel.

Fig. 3 shows typical voltage profiles of a stoichiometric spinel operated at different test temperatures (a, b) and after a soaking test at 70°C for 2 weeks (c). Fig. 3(a) and (b) show

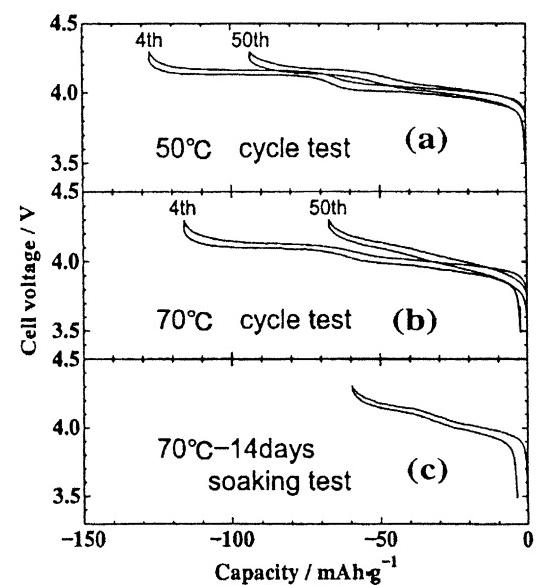


Fig. 3. Typical cycle behavior of LiMn_2O_4 spinel: (a) cycling at 50°C; (b) at 70°C; (c) First charge/discharge curve after LiMn_2O_4 was soaked in a 1 M LiPF_6 -EC/DMC (1:2 by volume) electrolyte for 2 weeks.

the 4 and 50th charge/discharge profiles of the stoichiometric spinel at 50 and 70°C, respectively. These show that the capacity loss in the low and high voltage regions depends on its operating temperature. The discharge capacity of the LiMn₂O₄ cycled at 50°C decreases from 66 to 52 mAh/g in the low voltage region and from 62 to 42 mAh/g in the high voltage region. The capacity retention rate in the high voltage region (68%) is much lower than that in the low voltage region (79%). However, when it was cycled at 70°C, the cells showed a capacity loss from 62 to 37 mAh/g in the low voltage region and from 53 to 32 mAh/g in the high voltage region. The capacity retention rate of the LiMn₂O₄ spinel at 70°C is almost the same at about 60% in both voltage regions. This means that the capacity loss of LiMn₂O₄ at high temperature happens in the high and low voltage regions at the same time.

It is also well-known that the capacity fading during cycling or storage at high temperature is commonly linked to the Mn dissolution [1]. Therefore, we did a soaking test of the stoichiometric LiMn₂O₄ spinel to investigate these correlations between Mn dissolution and operating temperature of our sample. The stoichiometric LiMn₂O₄ spinel was soaked in the highly purified electrolyte (LiPF₆–EC/DMC solution) for 2 weeks. The amount of Mn ions in the electrolyte was 32.0, 60.7 and 592 ppm at 50, 60 and 70°C, respectively. These values increase with the soak temperature increasing. It is also noticeable that the amount of dissolved Mn ion at 70°C is 10 times higher than at 60°C.

Fig. 3(c) shows the first charge/discharge curve of the stoichiometric spinel which had been soaked in electrolyte for 2 weeks. This profile is the 50th voltage profile curve

which was cycled at 70°C between 3.5 and 4.3 V. We now reconfirmed that the capacity loss of LiMn₂O₄ at high temperature simultaneously occurs in the low and high voltage regions. We concluded that the main reason for the capacity loss at elevated temperature is the decay of the spinel structure which resulted from a significant Mn dissolution.

4. Conclusion

LiMn₂O₄ has been synthesized at different calcination temperatures using the melt-impregnation method. It exhibited an oxygen deficient spinel structure over 800°C and showed a large 3.2 V plateau value in the discharge curve. We found that the 3.2 V plateau showed a very strong relation with the oxygen deficiency and could represent the degree of oxygen deficiency in the spinel structure. We also report that the capacity loss at high temperature occurs in both the high and low voltage regions, which is due to the decay of the spinel structure which resulted from a significant Mn dissolution.

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